

# The role of deposition sequence in cold spraying of dissimilar materials

R. Nikbakht<sup>a,b,\*</sup>, S.H. Seyedein<sup>b,\*</sup>, S. Kheirandish<sup>†c</sup>, H. Assadi<sup>d</sup>, B. Jodoin<sup>a</sup>

<sup>a</sup> Cold spray laboratory, Mechanical Engineering Department, University of Ottawa, 770 King Edward, Ottawa, Ontario, Canada, K1N 6N5

<sup>b</sup> Materials Processing Simulation Laboratory (MPS – Lab), School of Metallurgy and Materials Engineering, Iran University of Science and Technology (IUST), Narmak, Tehran, Iran

<sup>c</sup> School of Materials and Metallurgical Engineering, Iran University of Science and Technology, Narmak, Tehran, Iran

<sup>d</sup> Brunel Centre for Advanced Solidification Technology (BCAST), Brunel University London, Uxbridge, United Kingdom

## Abstract

Cold spraying of dissimilar materials have been addressed to understand the role of deposition sequence on the characteristics of the coating/substrate interface. Nickel and titanium coatings were sprayed onto the substrates of the opposite material under different conditions. The samples were subsequently heat treated, to better reveal the quality of metallic bonding at different locations, and examined by mechanical testing and microstructural analysis. The results show that the bonding characteristics of the Ni(coating)/Ti(substrate) pairs are significantly different from those of the

---

\* Corresponding author. Tel. +16135625800 Ext: 2481  
E-mail address: Roghayeh.Nikbakht@uottawa.ca

\* Corresponding author. Tel. +982177240319  
E-mail address: Seyedein@iust.ac.ir

† Deceased on 3 June 2018.

Ti(coating)/Ni(substrate) pairs. Mechanical interlocking and intermixing instabilities were observed only at the interfaces of the Ni/Ti pairs, which also showed a more uniform and higher fraction of intermetallics compared to the Ti/Ni pairs in similar spraying conditions. This was attributed to higher degrees of particle/substrate deformation in the Ni/Ti pair. Also, the bond strength of the Ni/Ti pair appeared to be almost three folds of the Ti/Ni pair (64.31 MPa vs. 22.8 MPa). These findings are considered to have implications in cold-spray additive manufacturing of hybrid components or bimetals.

Keywords: Cold spray, Coating, Dissimilar bonding, NiTi Intermetallics, Bond strength, Bimetals.

## 1. Introduction

Cold spraying (CS) is a powder consolidating technique for which powder particles are accelerated to high velocities (300 - 1200 m/s) by expanding a pressurized inert gas through a converging-diverging nozzle [1]. The kinetic energy of the particles mostly dissipates upon impact into heat and plastic deformation, contributing to particle bonding [2, 3]. High strain rates inherent to cold spray (from  $10^3$  to  $10^9$  s<sup>-1</sup>) result in adiabatic plastic deformation as the characteristic deformation time is not sufficient for adequate diffusion of the generated heat [4, 5], leading to localized thermal heating and material softening. This localized thermal softening can overcome strain hardening, resulting in adiabatic shear instability (ASI) [2, 4, 5]. The native superficial oxide layer breaks off as a result of this material flowing and severe plastic deformation [6-8]. The resulting conforming intimate contacts of particle/substrate and particle/particle interfaces under high pressure interact directly at the atomic scale allowing the development of a metallic bond between the impacting entities [9]. Assadi et al. [10] showed that ASI takes place at velocities around or beyond a critical velocity which is material and particle size dependent [5, 10, 11]. Velocity analysis of feedstock powders in cold spraying has demonstrated that for a typical particle size of CS (10–45 μm for ductile materials) smaller particles travel at faster speeds than larger particles [12] which might imply that small particles can easily reach their critical velocity of a given material. On the other hand, it has been reported that the variation of the particle velocity with particle size is not monotonic, i.e. under an optimal particle diameter for a given material particle impact velocity increases by increasing particle diameter, reaching a maximum (at the optimal particle diameter) and then decreasing with further increase of particle diameter [11, 13]. Then very fine particles (smaller than the optimal particle diameter) have low impact velocities as a result of deceleration due to the bow-shock wave that forms in front of the substrate which affects impact velocity of fine particles more effectively [13].

Schmidt et al. [5] showed that this optimal particle diameter (reaching maximum impact velocity) varies with material properties especially density in such a way that aluminium particle and copper particles respectively reach the maximum velocity at a particle diameter of 15 and 6  $\mu\text{m}$  [5]. Besides, very fine powders suffer from low deposition efficiency due to reduced flowability and self-agglomeration [14]. Furthermore, it has been demonstrated that smaller particles with their higher surface to volume ratio can experience hindered ASI resulting in increased critical velocity [5, 15]. Besides, in similar oxidation condition smaller particles (with an identical chemical composition) tend to have higher oxygen content due to the higher surfaces to volume which can influence bonding by increasing the critical velocity of particles [16].

The bond strength is also considered to be influenced by different interlocking mechanisms [17-20]. Wavy interfaces and vortex-like features (explained within the context of the Kelvin–Helmholtz instability phenomenon) may additionally contribute to the bond strength of some CS depositions [21-24]. This interfacial intermixing with roll-ups and vortices has been observed in CS deposits of high-density material such as Ni (onto Al) [24] and Cu (onto Al) [21]. This was found to stem from a large difference in velocities and densities of the lower and upper layers of the substrate surface due to the impact of the high-density material [25].

CS of dissimilar (particle/substrate) pairs introduces added complexity to the bonding mechanism analysis due to the differences in thermal and physical properties of the materials. According to their relative stiffness, hardness, and yield strength, CS of dissimilar pairs has been classified into soft/hard and hard/soft cases. Bae et al. [2] showed that for dissimilar pairs, plastic deformation of the softer counterpart is predominant. CS investigations of Cu/Al and Al/Cu pairs showed that the bond strength of the Cu/Al pair is drastically larger than that of the Al/Cu pair [26]. Bonding mechanisms of Cu/Al and Al/Cu pairs were investigated by Meng et al. in the context of hard/soft and soft/hard dissimilar pairs [27]. This study showed that in the soft/hard pair, the dominant

bonding mechanism was mostly related to the particle deformation and weak mechanical anchoring while for the hard/soft pair, mechanical interlocking was involved as well as substantial metallurgical bonding allowed by the large substrate deformation inducing oxide cleaning at the substrate [27]. The hard/soft classification used by Lee et al. [28] for mechanical matching investigation of Ni/Al and Al/Ni pairs showed that rough interface with interlocking features formed at the Ni/Al pair (hard/soft). Likewise, CS studies of hard/soft pairs of Ni/Al and Ti/Al showed that the harder Ni and Ti particles were embedded in Al substrates without much particle deformation, with the initial substrate roughness appearing to be insignificant. For the soft/hard pair of Al/mild steel, it was shown that the substrate roughness plays an important role in bonding as the soft Al powder particles were not able to deform the substrate [18]. Christoulis et al. showed that CS Ti particles on AISI 1050, Cu, AISI 304L, and Ti-6Al-4V substrates (respectively from the softest to hardest) resulted in particle embedment of un-deformed Ti particles for first two substrates, deformation of both particle/substrate for the third pair, and particle deformation with minimal substrate deformation for the last pair [29]. Furthermore, Bae et al. [2] showed CS Ni particles deposited on Al 6061-T6, Cu and SKH51 substrates respectively with particle embedment, particle embedment and particle deformation, and solely particle deformation.

Post-spray heat treatment (PSHT) of dissimilar pairs has been performed with different objectives. In some studies, PSHT for promoting interfacial intermetallic growth has been employed for metallurgical bonding assessment of CS deposits. Price et al. [30] and Hussein et al. [26] respectively explored the inter-particle and interfacial metallurgical bonding of CS Cu-Al composite (on a pure Cu substrate) and asymmetrical Cu/Al and Al/Cu pairs using intermetallics growth of heat-treated deposits. Additionally, Nastic et al. [31] evaluated the metallurgical part of the bond strength of aluminum coatings deposited on differently treated 300M steel substrate using PSHT and intermetallics growth method. Other studies have investigated PSHT of Al/Mg pair [32,

33], Al/Cu pair [34], and Ni/Al and Al/Ni pairs [28, 35] with the aim of bond strength improvement by interdiffusion and interfacial intermetallics formation. In this regard, Lee et al. found that spraying parameters (e.g. pressure) of CS Ni/Al pair and Ni-Al composite deposits influence phase formation kinetics and the precursor consumption during PSHT [28, 35]. The differences in morphology and formation kinetics of intermetallics in asymmetrical pairs were addressed either through deformation (defect) enhanced interdiffusion phenomenon which is likely to take place in CS in analogy with surface mechanical attrition treatment technique and mechanical alloying [35] or different bonding state of asymmetrical pairs (for instance Cu/Al and Al/Cu) [34].

In the previous work [36], PSHT and interfacial intermetallic growth were employed to analyse Ni/Ti and Ti/Ni single impact pairs. By direct correlation of highly strained areas of splat interfaces (predicted by simulation) with interfacial intermetallics pattern, it was shown that metallurgical bonds are likely to form at highly strained areas. It has been shown that morphology and kinetics of interfacial intermetallics formation in Ni-Ti system are influenced by the bonding state of the single splat. The current work extends this previous study of single impacts to complete layers of cold sprayed deposits, with implications in additive manufacturing of hybrid systems, e.g. to be used as preforms for the production of intermetallic components.

Ni-Ti alloy is well known and used for its shape memory and superelastic properties, thus making the Ni-Ti system of particular interest. Electroplating of pure Ti (and Ti alloys) with a nickel base and Ni-Ti composite [37-41], followed by heat treatment have been used to improve the limited wear resistance of Ti (and Ti alloys). Ni-Ti bimetallics are produced by explosive welding with potential application as electrodes in chlorine production industry where good bonding is essential for ensuring good electrical conductivity [42, 43]. In all mentioned applications, nickel and nickel-titanium composite coatings could potentially be deposited onto Ti and Ti alloys by the CS consolidation method which ensures to fulfil strong bond strength demands where the passivation

of titanium in electroplating process leads to a poor mechanical bonding and explosive welding is limited by the possible geometries. Further analysis of CS behaviour of Ni/Ti and Ti/Ni pair is thus of great practical as well as scientific importance for the production of hybrid components, or bimetals.

Single impact studies provide useful information on sprayability and deformation behaviour of individual particle/substrate pairs, but other factors incorporate in the deposition of coatings. Single particles generally are sprayed at low feeding rate and high traversing speed on a polished surface [44] while coatings are sprayed with a relatively lower traversing speed and higher feed rate. The lower traverse speed with longer heating time [45] allows more heat input to the coating and substrate. Therefore, the substrate in the single impact experiment experiences a different surface temperature, which can influence the deposited layer deformation process upon impact of new incoming particles [46].

Additionally, in single impact studies, the effect of a previous layer of coating (which is of importance especially in dissimilar pairs), peening effect of successive particle impacts and the effect of substrate surface roughness on coating deposition are not taken into account.

This study aims at investigating (beyond the simple single impact process) the CS processing of Ni/Ti and Ti/Ni systems, their respective bonding features and the potential production of Ni-Ti bimetals by CS consolidation method. Ni and Ti coatings were deposited respectively onto Ti (bulk or cold-sprayed) and Ni substrates. Particles and substrates deformation, as well as interface morphology of the etched coatings, were analysed to determine deposition characteristics of asymmetrical pairs. The contribution of different interface morphologies and deposition sequences on bond strength was evaluated by PSHT and interfacial intermetallics growth. Microhardness and bond strength of coatings are measured and fracture surface analysed, to correlate bond strength

with deformation, bonding mechanism and interfacial intermetallics growth, and to find common bonding features of Ni/Ti and Ti/Ni pairs with hard/soft and soft/hard dissimilar pairs.

## 2. Experimental procedures

Two spherical gas atomized Ni powders (CP-Ni, Atlantic Equipment Engineers, Upper Saddle River, NJ, USA) with two different particle size distribution (referred to as Ni-1 and Ni-2) and a spherical gas atomized Ti powder (CP-Ti, Advanced Powder and Coatings, Boisbriand, Canada) were used as feedstock materials. The nickel and titanium coatings were sprayed respectively onto 25.4mm×80mm×15mm flat substrates of Cp-Ti Grade 2 (ASTM B265) and Ni-200 (ASTM B162). Substrates for adhesion evaluation were machined into 25.4-mm-diameter cylinders in compliance with the ASTM C-633 adhesion strength standard. All substrates were ground, cleaned in an ultrasonic bath of ethanol and were dried using compressed air prior to the cold spraying. A digital optical microscope (VHX-2000 Keyence Corporation, Osaka, Japan) was used to generate a 3D profile of the four substrate surfaces (before coating deposition). The surface roughness was then calculated by analyzing the depth profiles through MATLAB which were in the range of 1.5μm for all four substrates.

CS coatings were produced using the commercially available EP Series SST Cold Spray System (Centerline (Windsor) Ltd., Windsor, Ontario, Canada). Details of the spray system can be found elsewhere [17, 47]. A stainless steel de Laval nozzle with the throat diameter, diverging section and exit diameter of respectively 2 mm, 120 mm and 6.6 mm was used. Both Ni powders were sprayed with nitrogen and Ti powder was sprayed with both nitrogen and helium to produce coatings which will hereafter be termed Ni-1, Ni-2, N<sub>2</sub>-Ti and He-Ti coatings. Furthermore, Ni-2 coatings were sprayed on cold-sprayed N<sub>2</sub>-Ti coatings to examine the layer by layer fabrication effect on the Ni/Ti pair. Prior to spraying Ni-2 coatings, the cold sprayed N<sub>2</sub>-Ti coatings were



machined to a nominal thickness of 1 mm followed by a surface preparation similar to bulk substrates surface preparation. The spraying parameters used in the current work are listed in Table 1.

Three samples of Ni-2 coating onto CP-Ti (Grade 2) and N<sub>2</sub>-Ti coating onto Ni-200 were sprayed for bond strength tests. After deposition, the adhesion strength samples were machined to a nominal thickness of 500 μm. The coatings adhesion strength was determined in compliance with the ASTM C-633 standard test method for adhesion/cohesion strength of thermal spray coatings. Samples average and standard deviation were computed and their fracture surface analysed using a scanning electron microscope (SEM) (EVO MA-10, Carl Zeiss AG, Oberkochen, Germany).

For intermetallics growth assessment, test samples were heat treated for 5 and 180 minutes at 700 °C in a vacuum furnace (with vacuum level below 10<sup>-6</sup> torr). The as-sprayed and heat treated cross-sectioned samples were prepared by standard metallography procedures. Etching of the coatings was carried out using Kroll's and Kaling's reagents for titanium and nickel coatings to highlight interparticle bonding. The polished and etched microstructures of as-sprayed coatings and heat-treated coatings were examined using SEM to allow further understanding of particle/substrate deformation, interface morphology and bonding.

Microhardness values of as-sprayed coatings were obtained using a Duramin-1 (Struers Inc., Cleveland, OH, USA) microhardness tester equipped with a Vickers indenter with a load of HV<sub>0.025</sub> and a dwell time of 10 s. The mean hardness value over ten readings was obtained for each sample.

### 3. Results and discussion

#### 3.1. Characteristics of Ni-1, Ni-2 and Ti powders

The morphology of Ni-1, Ni-2 and Ti feedstock powders are shown in Fig. 1a-c. SEM observations of the free-standing particles reveal the spherical morphology of all three powders with some satellites present. The powders size distribution measured by laser diffraction analysis (Microtrac model S3500, Montgomeryville, PA, USA) resulted in mean particle sizes of 6.63  $\mu\text{m}$ , 24.53  $\mu\text{m}$  and 30.66  $\mu\text{m}$  respectively for Ni-1, Ni-2, and Ti powders (Fig. 1d). The powder size distributions indicate that Ni-1 powder particles present a very small and tight size distribution, characterized by a  $D_{10}$  value of 5.05  $\mu\text{m}$ , a  $D_{50}$  value of 5.70  $\mu\text{m}$  and a  $D_{90}$  value of 6.19  $\mu\text{m}$ . Ni-2 powder particles present a  $D_{10}$  value of 15.51  $\mu\text{m}$ , a  $D_{50}$  value of 22.7  $\mu\text{m}$ , and a  $D_{90}$  value of 35.33  $\mu\text{m}$  while Ti powder particles present a  $D_{10}$  value of 17.65  $\mu\text{m}$ , the  $D_{50}$  value of 28.88  $\mu\text{m}$ , and  $D_{90}$  value of 44.85  $\mu\text{m}$ , showing slightly broader size distributions than Ni-1 powder.

#### 3.2. Microstructural and interfacial features of coatings

Cross-sectional SEM images of Ni-1, Ni-2, N<sub>2</sub>-Ti and He-Ti coatings are illustrated in Figs. 2a-d. Both Ni-1 and Ni-2 coatings present wavy interfaces including some local intermixing areas (close-up images of Figs. 2a and b). This observation differs from single impact studies [36] which showed that cold sprayed Ni particles predominantly deform with shallow penetration into the substrate, as shown schematically in profile image of Ni/Ti single impact in Fig. 3a. That study also reported large penetration to the substrate but only when particles were impacting on a crater left behind bounced-off particles. The relatively slower traversing speed of nozzle resulting in higher heat input might lead to higher substrate temperature and thus a higher level of substrate deformation in the build-up coating compared to the single impact test. Therefore, the large deformation level

of the Ti substrate underneath of Ni coatings observed in Fig. 2 allows concluding that they were roughened by the impinging Ni particles at potentially higher substrate temperature.

Rough interfaces generally have been observed in a hard/soft pair of dissimilar pairs and explained by physical trapping of hard particles in soft substrates. In the current dissimilar pair, the Ti substrate underneath of Ni coatings presents a rough interface where Ti is the hard part of the dissimilar pair (171 HV<sub>0.025</sub> vs. 146 HV<sub>0.025</sub>) [26, 27].

The interface morphology of both Ti coatings was similar to interface observations of single particle penetrations into Ni substrate (Figs. 2c-d and 3b-c) with a limited number of shallow craters observed on the Ni substrate underneath of Ti coatings (Figs. 2c and 3b). This indicates that Ni substrates of N<sub>2</sub>-Ti were almost non-deformed by incoming particles despite the fact that Ti particles are harder than Ni substrate (153 HV<sub>0.025</sub> vs. 117 HV<sub>0.025</sub>) and sprayed at slower gun speed than the single impact results reported previously [36].

It has been shown by laser measurements that for similar spraying conditions particles of Ni-2 and N<sub>2</sub>-Ti coatings have an almost similar range of impact velocities [36]. Considering the interface morphology of these two coating, it is evident that the Ti substrate of Ni-2 coating has a higher level of deformation compared to N<sub>2</sub>-Ti coating. While N<sub>2</sub>-Ti coating was sprayed with lower spray gun speed compared to Ni-2 coating, which means that Ni substrate of N<sub>2</sub>-Ti coating had a higher surface temperature, and was expected to have higher substrate deformation. This relative lower substrate deformation of N<sub>2</sub>-Ti coating can be addressed by the relatively lower mass density of Ti particles in N<sub>2</sub>-Ti/Ni pair (compared to Ni particles in Ni-2/Ti pair) and consequently lower kinetic energy of impacting particles.

The interface of Ni-1 coating presents a regular wave appearance with an amplitude (the distance between peaks and valleys) of about 5 μm while the Ni-2 coating has random wavy shape with an

amplitude of about 20  $\mu\text{m}$ . The amplitudes of the wavy interfaces of both coatings are respectively in the range of the mean particle size of the corresponding feedstock powders. The intermixing spots are more prevailing at the interface of Ni-1 coating than at the interface of Ni-2 coating. Considering the fact that high-density material like copper have lower optimal particle size (reported to be 6 $\mu\text{m}$  [5] and 1.5  $\mu\text{m}$  [13]) which can reach maximum impact velocity, it seems that Ni-1 powder with mean particle size of 6.63  $\mu\text{m}$  on average are large enough to be considered unaffected by bow shock effect. Then, for the same spraying conditions particles of finer Ni-1 powder were more likely to reach higher impact velocity, however, lower deposition efficiency was achieved for Ni-1 powder compared to that of Ni-2 powder (7% vs. 15%). Additionally, it is known that the ratio of particle impact velocity to critical velocity is a key parameter that controls deposition efficiency [48, 49]. This leads to rationalizing that the fine Ni-1 powder used in this work has a higher critical velocity compared to that of Ni-2 powder potentially due to the lack of adiabaticity [5] and more oxide content [16] of fine Ni-1 powder as a result of a higher surface to volume ratio of this powder.

Considering this point combined with the fact that there is almost no overlap between the particle size distributions of the two Ni powders (Fig. 1d), one can conclude that on average the Ni-1 powder particles succeeding to adhere to the substrate had potentially higher impact velocities compared to the Ni-2 powder particles that adhered to the substrate. These relatively higher impact velocity and lower deposition efficiency of Ni-1 powder seemed to intensify the intermixing phenomenon of Ni-1 coating interface.

Considering the fact that the intermixing phenomena and wavy interface were not observed for N<sub>2</sub>-Ti/Ni with a similar range of particle impact velocity of Ni-2 coating nor for He-Ti with higher impact velocity (associated with the use of He as a process gas at same spraying condition), it can

be inferred that relatively higher density of Ni particles of Ni/Ti pair is the cause of intermixing and wavy interface development as stated in the references [21-24].

Then, it can be stated that deposition efficiency and impact velocity, as well as relative density [21-24], play roles in the occurrence of intermixing phenomenon at the interface of the nickel coatings.

Figs.4a-d respectively show the etched microstructure of the various coatings. Nickel particles of both Ni coatings (Figs.4a and b) appeared to be well deformed and produced dense coatings. However, N<sub>2</sub>-Ti coating (Fig.4c) has a higher level of inter-particle porosity as a result of incomplete compaction. He-Ti coating (Fig.4d) appears to have a higher level of particle compaction and presents a lower porosity level, attributed to higher particle impact velocities associated with the use of helium as a process gas. Particles of Ni coatings completely lost their original spherical shape and deformed into a lens-like shape while the original spherical shape of particles of both N<sub>2</sub>-Ti and He-Ti coatings can be recalled to some extent.

### 3.3. Microhardness analysis

The extent of particles plastic deformation upon impact was evaluated by microhardness measurements. Fig.5 shows Vickers microhardness values of all three powders, Ni-1, Ni-2 and N<sub>2</sub>-Ti and He-Ti coatings, substrate materials and interface areas on the substrate side. As can be seen from the optical image of Ni deposits in Fig 5, the microhardness of deposits and the interfaces all were measured in a line with the same distance from the interface.

Ni-1 coating with a microhardness value of  $326 \pm 8 \text{ HV}_{0.025}$  showed the highest hardness among all four coatings. While sprayed at the same deposition conditions, the microhardness of Ni-2 coating was  $265 \pm 15 \text{ HV}_{0.025}$ . Higher microhardness of Ni-1 coating can be addressed through the fact that in a unit area of Ni-1 coating more Ni particles are impacting (same feed rate used but smaller particles) at higher speed compared to Ni-2 coating, thus increasing the cold working effect.

The microhardness of both titanium deposits ( $185\pm15$  and  $199\pm13$  HV<sub>0.025</sub> respectively for N<sub>2</sub> and He-sprayed Ti/Ni) appeared to be slightly higher than that of the feedstock titanium powder ( $153\pm20$  HV<sub>0.025</sub>). Despite the fact that the microhardness measurements of Ti coatings are challenging due to the presence of porosities, this small range of changes in microhardness values from powder to cold spray deposits can be expected due to limited deformation of titanium particles upon impact (considering deformation of the Ti particles in Figs.2c-d and Fig.4c-d). An increase of microhardness values was observed on the substrate side of the interface area relative to the substrate material for all cases. This can be attributed to dislocation-induced strengthening (i.e. work hardening).

---

#### 3.4. Effect of heat treatment on the interface microstructure

SEM images of as sprayed and heat treated Ni-2 coating are shown in Fig.6. The as-sprayed Ni-2 coating was etched to reveal the particle boundaries and grain distribution. The elongated and severely deformed grains are seen inside the particles (particle boundaries are marked in Fig. 6a). After heat treatment of Ni-2 coating for 5 minutes at 700 °C, interfacial intermetallic compounds (IIMCs) have formed. The elongated grains of as sprayed coating microstructure recrystallized and came in a new structure.

BSE images of the four coatings after being heat treated at 700 °C for 5 and 180 minutes are respectively presented in the left and right column of Fig.7. After being heat treated for 5 minutes at 700 °C, continuous layers of IIMCs grew at the interfaces of all coatings except for N<sub>2</sub>-Ti coating (Fig.7-c1) which failed to grow IIMCs in some interfacial areas. Having the lowest particle deformation and microhardness amongst the four coatings, N<sub>2</sub>-Ti coating grew the lower amount of IIMCs suggesting that formation of intermetallics at some interface areas of this coating had a larger incubation time due to the presence of an initial gap or oxide film on the reaction surfaces.

After being heat treated for 180 minutes at 700 °C (right column of Fig.7), the IIMCs of all coatings grew and their thickness (in the thickest area) measured to be almost 10 μm. EDS spectrum and analysis of IIMCs of marked points of Ni-2 coating (Fig.7-b2) are given in Fig.8 and Table 2. EDS analysis of the IIMCs showed Ti<sub>2</sub>Ni and Ni<sub>3</sub>Ti phases respectively formed in contact with Ti and Ni coating or substrate with NiTi phase formed in between of them which correlates with expected equilibrium phases [50].

Close-up images of Figs.7 (a1-b1 and a2-b2) showed that although interface areas of both Ni coatings are covered with IIMCs, the pattern and distribution of grown phases are different for the two coatings. A continuous layer of Ti<sub>2</sub>Ni phase formed at the interface of Ni-1 coating in contact with Ti substrate while Ni<sub>3</sub>Ti phase formed discontinuously (Fig.7-a1). At the interface area of Ni-2 coating, on the other hand, the Ti<sub>2</sub>Ni phase is absent in some spots while Ni<sub>3</sub>Ti phase formed a continuous layer (Fig.7-b1). This indicates that the Ni<sub>3</sub>Ti phase was the first intermetallics nucleating from interface areas of this coating. After the long annealing time, all three intermetallics became continuous at the interface of the Ni-2 coating (Fig.7-b2) while non-uniformity of IIMCs of Ni-1coating (Fig.7-b1) became pronounced and the Ni<sub>3</sub>Ti phase can be seen in few spots of the interface. From the close-up image of He-Ti coatings (Fig.7-d1 and d2), it seems that the thickness of the Ni<sub>3</sub>Ti phase changes with interface morphology (with particle penetration).

Comparing the thickness of the three intermetallics at the interface areas of all four coatings, NiTi phase formed the thickest layer of IIMCs, nonetheless the fact that Fig. 7-b1 showed NiTi phase forms after Ni<sub>3</sub>Ti phase formation. Then it can be concluded that NiTi phase is the fastest growing phase of all three intermetallics, as reported in the literature [51]. It can be inferred that formation of new Ni<sub>3</sub>Ti at the interface areas after nucleation of NiTi phase would not be favoured kinetically if the Ni<sub>3</sub>Ti phase fails to form a continuous layer at the early steps of phase formation. From the

above points, it seems that the morphology of the Ni<sub>3</sub>Ti phase is tightly related to the IIMCs formation ability and consequently metallurgical bonding state of the coatings/substrates interfaces.

Both Ni-1 and He-Ti coatings potentially had higher particle impact velocities and showed higher microhardness values compared to the other coating of the same pair. Thus as it is expected, He-Ti showed more uniform IIMCs compared to the N<sub>2</sub>-Ti while it is not the case for Ni-1 coatings. These can be explained by the fact that higher impact velocity in Ni-1 coating was accompanied by higher critical velocity as well. This means that the ratio of impact velocity to critical velocity plays the more important role in the development of metal-metal bonding than high velocity impacts alone.

Considering the asymmetrical pairs of Ni-2 and N<sub>2</sub>-Ti coatings (with close range of impact velocity and particle size distribution [36], and same stagnation gas pressure and temperature) Ni-2 presented quite continuous and uniform IIMCs compared to N<sub>2</sub>-Ti coating. This means that Ni-2 coating succeeded to develop a higher fraction of metallurgical bonding which can be attributed to higher deformability and higher kinetic energy stems from the higher mass density of Ni particles.

The growth of IIMCs is accompanied by the formation of micropores at the Ni/Ni<sub>3</sub>Ti interfaces which are more evident at the interface of N<sub>2</sub>-Ti and the intermix area of Ni-1 coatings (respectively Figs. 7-c1 and a1). The formation mechanism of micro-pores can be attributed to Kirkendall effect which has its origin in the difference of diffusion coefficient of titanium and nickel [42, 50], is inherent to Ni-Ti diffusion system. On the other hand, particle/substrate melding is not continuous at the whole interface area and the metallurgical bonding is more likely at the peripheral shear zone of particles [36] but even in these areas the metallurgically bonded spots are not continuous and some discontinuities were seen at metallurgically bonded areas [7, 36, 52].



The influence of layer by layer fabrication deposition sequence of Ni/Ti was examined by spraying Ni-2 coatings on bulk and cold-sprayed N<sub>2</sub>-Ti substrates. Interfaces of Ni-2 coatings sprayed on bulk and cold-sprayed N<sub>2</sub>-Ti substrates after heat treatment at 700 °C for 180 minutes are shown in Fig. 9a and b. Both coatings formed continuous layers of all three expected equilibrium phases of Ni-Ti binary system. Intermetallics layers of both coatings are found to have similar thicknesses. This means that spraying Ni coatings on both substrates results in negligible differences in terms of bonding characteristics and intermetallics growth. Consequently, the CS technique can be used for fabrication of either bimetal multilayer components of Ni/Ti with well-bonded layers.

### 3.5. Bond strength tests and fracture mechanisms

The thick and continuous layers of IIMCs observed in Ni-2 coating suggested the most uniform and relatively best interfacial bonding features amongst all four coatings. The N<sub>2</sub>-Ti coating with discontinuous IIMCs even after 180 minutes of heat treatment, on the other hand, suggests the most non-uniform bonding features among all coatings. For the sake of bond strength comparison, these two coatings were analysed using standard bond strength test method and the fracture surfaces were studied.

Bond strength values of the Ni-2 and N<sub>2</sub>-Ti coatings are given in Table 3. The values of N<sub>2</sub>-Ti coating on nickel substrate are lower (22.82 MPa) than those of Ni-2 coating onto titanium substrates (64.31 MPa).

As shown in Fig. 2b, the larger kinetic energy associated with a heavier nickel particle impacts promotes the wavy interface morphology of Ni-2 coating with roll-ups and vortex-like features. Such features, as it is reported for Cu/Al pair, may enhance the overall strength of interfacial Ni/Ti bonding by increasing coating/substrate interface areas, fine length scale mixing of nickel coating and titanium substrate and mechanical interlocking of nickel particles into titanium substrate [23].

This bonding mechanism seems to have no contribution to the bond strength of N<sub>2</sub>-Ti coating as it presents an almost flat interface morphology. The interfacial intermetallics growth morphologies of Ni-2 and N<sub>2</sub>-Ti coatings showed that metallurgical bonding has more contributions to the bond strength values of Ni-2 coating compared to N<sub>2</sub>-Ti coating.

The bond strength values of cold sprayed Ni/Ti and Ti/Ni pairs are not reported in the literature at present. In comparison to the bond strength values of Al/Cu pair that is significantly lower than that for Cu/Al pair (1.1 Mpa vs 57.4 Mpa) [26], the bond strength difference of N<sub>2</sub>-Ti and Ni-2 coatings (22.8 MPa vs. 64.31 MPa) is less drastic. In the Ti/Ni pair, the nickel substrate is analogous to the copper substrate of the Al/Cu pair, with the same FCC crystal structure, high density and close range of specific heat. Then the higher bond strength of Ti/Ni pair compared to Al/Cu pair should be attributed to differences of spraying particle properties of two pairs. Ti particles of Ti/Ni pair have higher density and lower heat conductivity and specific heat relative to the aluminium particles of Al/Cu pair where all these properties have constructive roles on sprayability and bond strength of coatings. The HCP crystal structure of titanium particles and its higher melting point compared to Aluminum particles with lower melting point and FCC crystal structure hampers the deformability of Ti particle of Ti/Ni pair (Table 4).

The SEM images of fracture surfaces resulting from the bond strength tests are shown in Fig. 10. The substrate side of fracture surfaces (at two magnifications), cross-sections of fractures surfaces (substrate sides), and the corresponding deposit surfaces are shown respectively in the left and right columns of Fig.10 for N<sub>2</sub>-Ti/Ni and Ni-2/Ti pairs. From the BSE image of the fracture surface of nickel substrates (Fig.10-a1), remnants of individual and colonies of titanium particles are distinguishable at the substrate with grey contrast, while the fracture surface of the titanium substrate (Fig10-b1) are covered by well deformed and flattened nickel particles. These results indicate that both N<sub>2</sub>-Ti and Ni-2 coatings failed in mixed cohesion/adhesion mode near the

interface. Nonetheless, the failure mechanism of the titanium coating is mainly adhesive failure in contrast to the nickel coating where cohesive failure mechanism is predominant.

The magnified SE image of the nickel substrate (Fig.10-a2) demonstrates that the titanium particle penetration depths are shallow. The cross-section image of the fracture surface of the nickel substrate (Fig.10-a3) reveals that the impact-induced continuous layer of material at the interface area which is well distinguishable from the large grains of the original nickel substrate. Looking at the magnified BSE image of this distorted layer, equiaxed and gradient microstructural features from the interface towards the nickel substrate are evident. These microstructural features in combination with the increasing microhardness of the interface (Fig. 5) support the notion that grain refinement due to dynamic recrystallization or dynamic recovery may play a role in the microstructure alteration of the nickel substrate as well as the work-hardening effect of accumulated dislocations.

The close-up view of the fracture surface of the titanium substrate (Fig.10-b2) includes peak and valley features. The cross-section image of this fracture surface (Fig.10-b3) shows a rough fracture surface as well. A magnified image of one of those valleys shows a mixture failure mode of the trans-granular and inter-granular fracture at the titanium substrate (Fig.10-b2). Tracking the adhesion failure spots from the cross-section image of the fracture surface in Fig. 10-b3 confirms that fracture took place at the substrate side of the interface and some titanium fragments remained at the coating side. This implies that either local metallurgical bonding of the nickel/titanium was stronger than the strength of the titanium substrate or the interface of the titanium substrate influenced by high velocity impacts.

The coating side of the fracture surface of N<sub>2</sub>-Ti/Ni in Fig.10-a4 indicates almost a flat surface at which deformation and boundaries of individual titanium particles are distinguishable and the

fragments of the nickel substrate at the back of the coating are evident (Magnified image). The nickel coating (Fig.10-b4), on the other hand, imitates the same peak and valley morphology of the substrate side. Looking at this image, it is evident that nickel particles well deformed, flattened and coalesced. The coating fragments at the fracture surface of the substrate and substrate fragments at the fracture surface of the coating were seen which appear to suggest the possibility of metallic bond.

### 3.6. Bond strength and IIMCs growth in correlation to the sequence of bimetal Ni-Ti deposition

Ni-2 coating compared with He-Ti showed more uniform IIMCs which reveals more uniform bonding state of this coating which can be addressed by particle/substrate deformation. Development of metallic band relies on oxide layer break-off and removal which is directly related to the extent of (particle/substrate) deformation and jetting phenomenon occurring as a result of ASI [27, 53]. The native oxide layer of well deformed and flattened nickel splats of Ni-2 coating in comparison with both Ti coatings is most likely to be disrupted (Figs. 2-4 and 10).

The well-bonded Ni-2 coating has a thick and continuous layer of  $\text{Ni}_3\text{Ti}$  while N<sub>2</sub>-Ti with lower metallic efficiency shows a very thin layer of  $\text{Ni}_3\text{Ti}$  even in the intermetallics grown spots of the interface area. This is in correlation with  $\text{Ni}_3\text{Ti}$  phase growth morphology of the single impact experiments where  $\text{Ni}_3\text{Ti}$  intermetallics formed a thick layer at highly strained and metallurgically bonded areas of Ti splat/Ni substrate while it was absent or very thin at the rest of the interface [36]. Then it is evident that the bonding state influences the phase formation kinetics.

The bond strength analyses and interface morphologies of as-sprayed and heat-treated samples (Table 3, Figs.2-7 and 9) showed that cold sprayed Ni-Ti pairs fulfill strong bond strength demands of bimetals and hybrid components while there are no concerns about thickness and geometry of the layers to be sprayed in CS despite the other (solid-solid interface) bimetal production methods

like explosive welding. Then, based on the prospective demand for Ni-Ti bimetallics or hybrid components, bilayers or multilayer components of Ni-Ti could be produced by CS. CS investigation showed that different bonding characteristics, IIMCs morphologies and bond strength values were achieved (Table 3) for Ni/Ti and Ti/Ni pairs in the same spraying condition with the similar range of impact velocities which mean that the deposition sequence of dissimilar materials results in different bonding quality. Ti-Ni bimetallics can be produced either by spraying of Ni or Ti powders on the bulk dissimilar substrate or by spraying of two elemental powders in sequence to a dummy substrate. Findings of the research showed that spraying of Ni on Ti leads to the better bond strength and IIMCs morphologies compared to spraying of Ti on Ni substrates. Then in same spraying conditions, spraying of Ni powder to the bulk or already sprayed Ti substrate will lead to better results.

#### 4. Conclusion

The bonding phenomena of cold sprayed titanium onto nickel substrate and nickel onto titanium substrate have been studied experimentally. Two coatings were sprayed for each pair respectively with two Ni powders for the Ni/Ti pair and with two process gases (N<sub>2</sub> and He) for the Ti/Ni pair. Particle/substrate deformation and as sprayed interface morphologies of all coatings were analysed to learn about the influence of the deposition sequence of dissimilar material on respective bonding mechanisms of Ni-Ti bimetallics. The degree of metallurgical bonding formed in the Ni deposit–Ti substrate was compared to that of the Ti deposit–Ni substrate by interfacial intermetallics growth assessment. Bond strength tests and fracture surfaces analyses were conducted. Results are obtained from this study are summarized as follows:

1. Ni/Ti coatings showed wavy interfaces with mechanical interlocking and intermixing instabilities with the wave amplitude in the range of mean particle size while both Ti coatings presented interface roughness similar to single particle impact penetration. The

wavy and rough appearance of Ni/Ti interfaces was found to be intensified by the successive impact of Ni particles as particle deformation was dominant over substrate deformation at single impact experiments of Ni particles.

2. Higher areas exhibiting metallurgical bonding were achieved for the Ni/Ti pair (Ni-2 coating) compared to the Ti/Ni pair (N<sub>2</sub>-Ti) in same spraying condition. With the increase of impact velocity, the metallurgically bonded areas of He-Ti coating on Ni substrate was increased in comparison to N<sub>2</sub>-Ti coating. Larger areas exhibiting metallurgical bonding were observed for Ni-2 coatings with the medium particle size in comparison to Ni-1 coating produced using finer Ni-1 particles.
3. Higher bond strength values were achieved for Ni-2 coating compared with those of N<sub>2</sub>-Ti coating (64.31 MPa vs. 22.8 MPa). This was found to originate from the wavy interface with mechanical interlocking and a higher fraction of metallurgical bonding of Ni-2 coating which is in good agreement with microhardness and fracture surface results.
4. Interfacial intermetallic growth morphology is strongly influenced by the bonding state of the coatings. Well-bonded coating of each pair showed more uniform and continuous intermetallics layer including Ni<sub>3</sub>Ti phase while it is not the case for the other coating of each pair.
5. Cold spraying of Ni-Ti pairs ensures to fulfil strong bond strength demand for bimetals. Findings of this research suggest that for Ni-Ti bilayer production out of Ni and Ti powder, in same spraying conditions, spraying of Ni powder to the bulk or already sprayed Ti substrate will lead to better results.

## References

- [1] A. Papyrin, V. Kosarev, S. Klinkov, A. Alkimov, V. Fomin, Chapter 5 - Current status of the cold spray process, *Cold Spray Technology*, Elsevier, Oxford, 2007, pp. 248-323.
- [2] G. Bae, Y. Xiong, S. Kumar, K. Kang, C. Lee, General aspects of interface bonding in kinetic sprayed coatings, *Acta Mater.* 56 (2008) 4858-4868.
- [3] J. Kim, C. Lee, Correlation of Impact Conditions, Interface Reactions, Microstructural Evolution, and Mechanical Properties in Kinetic Spraying of Metals: A Review, *J. Therm. Spray Technol.* 25 (2016) 1461-1489.
- [4] M. Grujicic, C.L. Zhao, W.S. DeRosset, D. Helfrich, Adiabatic shear instability based mechanism for particles/substrate bonding in the cold-gas dynamic-spray process, *Mater. Des.* 25 (2004) 681-688.
- [5] T. Schmidt, F. Gärtner, H. Assadi, H. Kreye, Development of a generalized parameter window for cold spray deposition, *Acta Mater.* 54 (2006) 729-742.
- [6] Y. Xiong, G. Bae, X. Xiong, C. Lee, The Effects of Successive Impacts and Cold Welds on the Deposition Onset of Cold Spray Coatings, *J. Therm. Spray Technol.* 19 (2009) 575-585.
- [7] Y. Xie, S. Yin, C. Chen, M.-P. Planche, H. Liao, R. Lupoi, New insights into the coating/substrate interfacial bonding mechanism in cold spray, *Scripta Mater.* 125 (2016) 1-4.

- [8] H. Assadi, H. Kreye, F. Gärtner, T. Klassen, Cold spraying—a materials perspective, *Acta Mater.* 116 (2016) 382-407.
- [9] T. Hussain, Cold spraying of titanium: a review of bonding mechanisms, microstructure and properties, *Key Engineering Materials*, Trans Tech Publ, 2013, pp. 53-90.
- [10] H. Assadi, F. Gärtner, T. Stoltenhoff, H. Kreye, Bonding mechanism in cold gas spraying, *Acta Mater.* 51 (2003) 4379-4394.
- [11] H. Assadi, T. Schmidt, H. Richter, J.-O. Kliemann, K. Binder, F. Gärtner, T. Klassen, H. Kreye, On Parameter Selection in Cold Spraying, *J. Therm. Spray Technol.* 20 (2011) 1161-1176.
- [12] D. Goldbaum, J.M. Shockley, R. Chromik, A. Rezaeian, S. Yue, J.-G. Legoux, E. Irissou, The Effect of Deposition Conditions on Adhesion Strength of Ti and Ti6Al4V Cold Spray Splats, *J. Therm. Spray Technol.* 21 (2012) 288-303.
- [13] D. Helfritch, V. Champagne, A model study of powder particle size effects in cold spray deposition, ARMY RESEARCH LAB ABERDEEN PROVING GROUND MD, 2008.
- [14] R.N. Raoelison, Coeval Cold Spray Additive Manufacturing Variances and Innovative Contributions, *Cold-Spray Coatings*, Springer2018, pp. 57-94.
- [15] P.C. King, M. Jahedi, Relationship between particle size and deformation in the cold spray process, *Appl. Surf. Sci.* 256 (2010) 1735-1738.
- [16] C.J. Li, H.T. Wang, Q. Zhang, G.J. Yang, W.Y. Li, H.L. Liao, Influence of Spray Materials and Their Surface Oxidation on the Critical Velocity in Cold Spraying, *J. Therm. Spray Technol.* 19 (2009) 95-101.
- [17] R. Fernández, D. MacDonald, A. Nastić, B. Jodoin, A. Tieu, M. Vijay, Enhancement and Prediction of Adhesion Strength of Copper Cold Spray Coatings on Steel Substrates for Nuclear Fuel Repository, *J. Therm. Spray Technol.* 25 (2016) 1577-1587.
- [18] S. Kumar, G. Bae, C. Lee, Influence of substrate roughness on bonding mechanism in cold spray, *Surf. Coat. Technol.* 304 (2016) 592-605.
- [19] T. Hussain, D.G. McCartney, P.H. Shipway, D. Zhang, Bonding Mechanisms in Cold Spraying: The Contributions of Metallurgical and Mechanical Components, *J. Therm. Spray Technol.* 18 (2009) 364-379.



- [20] S. Yin, Y. Xie, X. Suo, H. Liao, X. Wang, Interfacial bonding features of Ni coating on Al substrate with different surface pretreatments in cold spray, *Materials Letters* 138 (2015) 143-147.
- [21] V.K. Champagne, D. Helfritch, P. Leyman, S. Grendahl, B. Klotz, Interface Material Mixing Formed by the Deposition of Copper on Aluminum by Means of the Cold Spray Process, *J. Therm. Spray Technol.* 14 (2005) 330-334.
- [22] M. Grujicic, J.R. Saylor, D.E. Beasley, W. DeRosset, D. Helfritch, Computational analysis of the interfacial bonding between feed-powder particles and the substrate in the cold-gas dynamic-spray process, *Appl. Surf. Sci.* 219 (2003) 211-227.
- [23] M. Grujicic, Particle/substrate interaction in the cold-spray bonding process, *The cold spray materials deposition process*. Woodhead Publishing Ltd, Cambridge (2007) 148-177.
- [24] L. Ajdelsztajn, J.M. Schoenung, B. Jodoin, G.E. Kim, Cold spray deposition of nanocrystalline aluminum alloys, *Metall. Mater. Trans. A* 36 (2005) 657-666.
- [25] D. MacDonald, A. Nastic, B. Jodoin, Understanding Adhesion, in: P. Cavaliere (Ed.), *Cold-Spray Coatings: Recent Trends and Future perspectives*, Springer International Publishing, Cham, 2018, pp. 421-450.
- [26] T. Hussain, D.G. McCartney, P.H. Shipway, Bonding between aluminium and copper in cold spraying: story of asymmetry, *Mater. Sci. Technol.* 28 (2013) 1371-1378.
- [27] F. Meng, D. Hu, Y. Gao, S. Yue, J. Song, Cold-spray bonding mechanisms and deposition efficiency prediction for particle/substrate with distinct deformability, *Mater. Des.* 109 (2016) 503-510.
- [28] H. Lee, S. Lee, H. Shin, K. Ko, Mechanical matching and microstructural evolution at the coating/substrate interfaces of cold-sprayed Ni, Al coatings, *J. Alloys Compd.* 478 (2009) 636-641.
- [29] D.K. Christoulis, S. Guetta, V. Guipont, M. Jeandin, The Influence of the Substrate on the Deposition of Cold-Sprayed Titanium: An Experimental and Numerical Study, *J. Therm. Spray Technol.* 20 (2011) 523-533.
- [30] T.S. Price, P.H. Shipway, D.G. McCartney, E. Calla, D. Zhang, A Method for Characterizing the Degree of Inter-particle Bond Formation in Cold Sprayed Coatings, *J. Therm. Spray Technol.* 16 (2007) 566-570.

- [31] A. Nastic, M. Vijay, A. Tieu, S. Rahmati, B. Jodoin, Experimental and Numerical Study of the Influence of Substrate Surface Preparation on Adhesion Mechanisms of Aluminum Cold Spray Coatings on 300M Steel Substrates, *J. Therm. Spray Technol.* 26 (2017) 1461–1483.
- [32] H. Bu, M. Yandouzi, C. Lu, B. Jodoin, Effect of heat treatment on the intermetallic layer of cold sprayed aluminum coatings on magnesium alloy, *Surf. Coat. Technol.* 205 (2011) 4665-4671.
- [33] Q. Wang, D. Qiu, Y. Xiong, N. Birbilis, M.-X. Zhang, High resolution microstructure characterization of the interface between cold sprayed Al coating and Mg alloy substrate, *Appl. Surf. Sci.* 289 (2014) 366-369.
- [34] J. Won, J. Kim, S. Lee, C. Lee, S. Lee, S.J. Kim, Effect of intermetallic compounds on the bonding state of kinetic sprayed Al deposit on Cu after heat-treatment, *Surf. Coat. Technol.* 302 (2016) 39-46.
- [35] H. Lee, H. Shin, K. Ko, Effects of Gas Pressure of Cold Spray on the Formation of Al-Based Intermetallic Compound, *J. Therm. Spray Technol.* 19 (2010) 102-109.
- [36] R. Nikbakht, S.H. Seyedein, S. Kheirandish, H. Assadi, B. Jodoin, Asymmetrical bonding in cold spraying of dissimilar materials, *Appl. Surf. Sci.* 444 (2018) 621-632.
- [37] M. Dabalà, K. Brunelli, R. Frattini, M. Magrini, Surface hardening of Ti – 6Al – 4V alloy by diffusion treatment of electroless Ni – B coatings, *Surf. Eng.* 20 (2014) 103-107.
- [38] G. Khosravi, M.H. Sohi, H.M. Ghasemi, A.K. Vafadar, Characterisation of Ni–Ti intermetallic coatings formed on Cp titanium by diffusion treatment, *International Journal of Surface Science and Engineering* 9 (2015) 43-54.
- [39] I. Rampin, K. Brunelli, M. Dabalà, M. Magrini, Effect of diffusion of Ni and B on the microstructure and hardness of Ti Cp, *J. Alloys Compd.* 481 (2009) 246-253.
- [40] Y. Zhao, C. Jiang, Z. Xu, F. Cai, Z. Zhang, P. Fu, Microstructure and corrosion behavior of Ti nanoparticles reinforced Ni–Ti composite coatings by electrodeposition, *Mater. Des.* 85 (2015) 39-46.
- [41] X. Zhou, Y. Shen, A novel method designed for electrodeposition of nanocrystalline Ni coating and its corrosion behaviors in Hank's solution, *Appl. Surf. Sci.* 324 (2015) 677-690.
- [42] K. Topolski, P. Wiciniński, Z. Szulc, A. Gałka, H. Garbacz, Progress in the characterization of explosively joined Ti/Ni bimetals, *Mater. Des.* 63 (2014) 479-487.

- [43] M. Aghasibeig, H. Monajatizadeh, P. Bocher, A. Dolatabadi, R. Wuthrich, C. Moreau, Cold spray as a novel method for development of nickel electrode coatings for hydrogen production, *International Journal of Hydrogen Energy* 41 (2016) 227-238.
- [44] X. Chu, R. Chakrabarty, H. Che, L. Shang, P. Vo, J. Song, S. Yue, Investigation of the feedstock deposition behavior in a cold sprayed 316L/Fe composite coating, *Surf. Coat. Technol.* 337 (2018) 53-62.
- [45] A.W.-Y. Tan, W. Sun, Y.P. Phang, M. Dai, I. Marinescu, Z. Dong, E. Liu, Effects of Traverse Scanning Speed of Spray Nozzle on the Microstructure and Mechanical Properties of Cold-Sprayed Ti6Al4V Coatings, *J. Therm. Spray Technol.* 26 (2017) 1484-1497.
- [46] Z. Arabgol, M. Villa Vidaller, H. Assadi, F. Gärtner, T. Klassen, Influence of thermal properties and temperature of substrate on the quality of cold-sprayed deposits, *Acta Mater.* 127 (2017) 287-301.
- [47] D. MacDonald, R. Fernández, F. Delloro, B. Jodoin, Cold Spraying of Armstrong Process Titanium Powder for Additive Manufacturing, *J. Therm. Spray Technol.* 26 (2016) 598–609.
- [48] W. Wong, P. Vo, E. Irissou, A.N. Ryabinin, J.G. Legoux, S. Yue, Effect of Particle Morphology and Size Distribution on Cold-Sprayed Pure Titanium Coatings, *J. Therm. Spray Technol.* 22 (2013) 1140-1153.
- [49] X.-J. Ning, J.-H. Jang, H.-J. Kim, The effects of powder properties on in-flight particle velocity and deposition process during low pressure cold spray process, *Appl. Surf. Sci.* 253 (2007) 7449-7455.
- [50] G.F. Bastin, G.D. Rieck, Diffusion in the titanium-nickel system: I. occurrence and growth of the various intermetallic compounds, *Metall. Trans.* 5 (1974) 1817-1826.
- [51] P. Novák, P. Pokorný, V. Vojtěch, A. Knaislová, A. Školáková, J. Čapek, M. Karlík, J. Kopeček, Formation of Ni–Ti intermetallics during reactive sintering at 500–650 °C, *Materials Chemistry and Physics* 155 (2015) 113-121.
- [52] K. Kang, S. Yoon, Y. Ji, C. Lee, Oxidation dependency of critical velocity for aluminum feedstock deposition in kinetic spraying process, *Mater. Sci. Eng., A* 486 (2008) 300-307.

[53] Y. Xie, M.-P. Planche, R. Raelison, P. Hervé, X. Suo, P. He, H. Liao, Investigation on the influence of particle preheating temperature on bonding of cold-sprayed nickel coatings, *Surf. Coat. Technol.* 318 (2016) 99-105.

Table 1

Spraying parameters of coatings.

Substrates	Feedstock powder	Stagnation gas	Temperature (°C)	Pressure (MPa)	Standoff Distance(mm)	Traverse Speed(mm)	Feeding Rate(g/m)	Passes Number
CP-Ti G2	CP-Ni-1	N <sub>2</sub>	500	3.4	15	5	7.2	8
CP-Ti G2	CP-Ni-2	N <sub>2</sub>	500	3.4	15	5	7.2	4
Sprayed-Ti	CP-Ni-2	N <sub>2</sub>	500	3.4	15	5	7.2	4
Ni-200	CP-Ti-G1	N <sub>2</sub>	500	3.4	15	1	6.5	2
Ni-200	CP-Ti-G1	He	500	3.2	15	1	6.5	1

Table 2

EDS analysis of Ni-2 coating of Fig. 7b-2 heat treated for 180 min at 700 °C.

No.	Ni at. %	Ti at. %	Phase
1	100	0	Ni
2	98.9	1.1	Solid solution Ni(Ti)
3	75.1	24.9	Ni <sub>3</sub> Ti
4	49.7	50.3	NiTi
5	33.5	66.5	Ti <sub>2</sub> Ni
6	0.9	99.1	Solid solution Ti(Ni)

Table 3

Bond strength values for N<sub>2</sub>-sprayed Ti/Ni pair and Ni/Ti pair.

Coating	Substrate	Spraying parameters	Bond strength (MPa)	Failure mode
Titanium	Ni-200	N <sub>2</sub> , T=500 °C, P= 3.4 MPa	22.82± 2.87	Mixed cohesion-adhesion
Nickel	Cp-Ti	N <sub>2</sub> , T=500 °C, P= 3.4 MPa	64.31± 10.61	Mixed cohesion-adhesion

Table 4

Materials properties

Property	unit	symbol	Al	Cu	Ni	Ti
Density	kg/m <sup>3</sup>	$\rho$	2699	8960	8908	4500
Conductivity	W/m/K	k	204	385	91	21
Crystal structure	-	-	FCC	FCC	FCC	HCP
Melting point	K	$T_m$	933	1350	1726	1941
Specific heat	J/kg/K	$C_p$	900	385	461	523
Yield strength	MPa	$\sigma_y$			82.7*	275*

\*Substrate material

### List of Figur Captions

**Fig. 1.** SEM micrograph of (a) spherical Ni-1 powder, (b) spherical Ni-2 powder, and (c) spherical Ti powder, and (d) measured particle size distribution of feedstock powders.

**Fig. 2.** SEM micrograph of as-sprayed coatings. (a), (b) and (c) respectively Ni-1, Ni-2 and N<sub>2</sub>-Ti coatings sprayed at T=500 °C and P=3.4 MPa with N<sub>2</sub> gas, and (d) He-Ti coating sprayed at T=500 °C and P=3.2 MPa with helium gas as a propellant gas.

**Fig. 3.** Schematic image of single impact profiles of Ni-2, N<sub>2</sub>-Ti and He-Ti respectively from (a) to (c) achieved from single impact experiments [36].

**Fig. 4.** SEM images of etched microstructures of coatings show particles deformation. (a) Ni-1 coating, (b) Ni-2 coating, (c) N<sub>2</sub>-Ti coating and (d) He-Ti coating. Ni and Ti coatings were respectively etched using Kaling's and Kroll's reagents.

**Fig. 5.** (a) Optical micrograph of the nickel coating onto titanium substrate showing the positions of micro-hardness measurements. (b) Vickers microhardness measured for all feedstock powders, coatings, substrates and interfaces.



**Fig. 6.** SEM image of as sprayed and heat treated (5 min at 700 °C) Ni-2 coating in (a) and (b). The as-sprayed coating is etched to reveal grain distribution and particle boundaries (marked with dash lines).

**Fig. 7.** Cross-sectional SEM image of the Ni-1, Ni-2, N<sub>2</sub>-Ti and He-Ti coatings after annealing treatment at the temperature of 700 °C for 5 min (left column) and 180 min (right column).

**Fig. 8.** EDS spectrum of Marked points of Ni-2 coating (Fig. 7-b2) after heat treatment at 700 °C for 180 min.

**Fig. 9.** Cross-sectional SEM image of the Ni-2 coatings sprayed on different Ti substrates after annealing treatment at the temperature of 700 °C for 180 min. (a) Bulk Ti substrate and (b) cold-sprayed N<sub>2</sub>-Ti substrate.

**Fig. 10.** The fracture surfaces of bond strength tests. (a1) and (b1) respectively show the substrate side of the fracture surface of N<sub>2</sub>-Ti/Ni and Ni-2/Ti pairs. (a2) and (b2) show respectively (a1) and (b1) at higher magnifications. (a3) and (b3) present cross-section image of (a1) and (b1). (a4) and (b4) indicate coating side of fracture surfaces of N<sub>2</sub>-Ti and Ni-2 coatings.